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16. ABSTRACT

Ambient concentrations of fine particle extracted organic matter (EOM) measured at the Elm Grove Park and Fire Station sites in Boise have been apportioned to their two principal sources, woodsmoke and motor vehicle emissions. A multiple linear regression method using lead and potassium-based tracers for motor vehicles and woodsmoke, respectively, was employed in the source apportionment. On average woodsmoke was found to be the dominant contributor to EOM at both sites and during both day and night. In spite of the 90% reduction in the lead content of leaded gasoline in the U.S., which has been in effect since January 1986, lead still appears to be a viable tracer of motor vehicle emissions.

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Ambient concentrations of fine particle extracted organic matter (EOM) measured at the Elm Grove Park and Fire Station sites in Boise have been apportioned to their two principal sources, woodsmoke and motor vehicle emissions. A multiple linear regression method using lead and potassium-based tracers for motor vehicles and woodsmoke, respectively, was employed in the source apportionment. On average woodsmoke was found to be the dominant contributor to EOM at both sites and during both day and night. In spite of the 90 % reduction in the lead content of leaded gasoline in the U.S., which has been in effect since January 1986, lead still appears to be a viable tracer of motor vehicle emissions.

## Introduction

In airsheds whose atmospheric mass loadings are dominated by woodsmoke and mobile source emissions, extractable organic matter (EOM) generally constitutes 50 % or more of the fine particle ambient mass concentration. The EOM is also the portion of the ambient aerosol which is associated with mutagenicity. For both reasons it is of interest to determine the percentage of measured EOM which is separately contributed by each of these expected sources, as well as any other less obvious ones. In past IACP studies in Albuquerque and Raleigh a multiple linear regression (MLR) approach, using Pb and K-based tracers for motor vehicle and woodsmoke sources, respectively, has been very successful in the source apportionment of EOM (and mutagenicity). However, since 1985 when the previous studies were conducted, a significant change has occurred in the Pb emissions of motor vehicles, related to the nationwide 90 % reduction in the Pb content of leaded gasoline. In the following we present source apportionment results for EOM measured during the recent IACP Boise study, with particular attention to the current viability of Pb as a tracer of motor vehicle emissions.

## Experimental

Field sampling and sample analyses followed closely the methods used in previous IACP studies[1,2]. Samples were collected at a residential site (Elm Grove Park - EGP) and a roadway site (Fire Station - FS) from November 1986 to February 1987. Samples for EOM analysis were collected on Teflon-coated glass fiber filters, using multiple Hi-vol samplers equipped with impactors whose cutpoint was 2.5 μm aerodynamic dia. A dichotomous sampler collected fine (0 - 2.5 μm dia) and coarse (2.5 - 10 μm dia) particles on separate Teflon filters which were subsequently analyzed for trace elemental composition by x-ray fluorescence. All samplers were operated on the same 12-h day (7 am - 7 pm) and night schedule. From the 60 - 70 sampling periods available in each of the four site - diurnal categories (two sites, day and night), chemometric considerations[3] were used to choose 25 each for EOM measurements. For the selected 100 sampling periods EOM measurements were performed following Soxhlet extraction with dichloromethane.

## Receptor Modeling

The source apportionment of EOM was performed with a single element tracer MLR model of the form

$$EOM_i = a\,(\text{Woodsmoke tracer})_i + b\,(\text{Motor vehicle tracer})_i + c \qquad (1)$$

where the subscripted quantities are measured simultaneously during each sampling period i, and the initially unknown coefficients a, b, and c, are determined by MLR using data from all the sampling periods together. The measured concentration of a tracer for sampling period i multiplied by its coefficient is the best estimate of the corresponding source's contribution to total EOM concentration during that sampling period. The intercept c can be regarded either as the average contribution of additional unknown sources, or as a measure of inadequacy of a two-source model. For either interpretation c should be small (relative to the average value of EOM) for an acceptable model.

As in previous work[1] a soil-corrected fine particle potassium tracer was used for woodsmoke:

$$K^*_i = K_i - Fe_i\,(K/Fe)_{soil} \qquad (2)$$

where the soil ratio was 0.72 ± 0.09 (mean ± std dev), as determined from the average K/Fe ratio in the coarse dichotomous samples. The same ratio was

found at both sites. Previous work in Denver[4], Albuquerque[1] and Raleigh[2] has given soil ratios of 0.68, 0.45, and 0.42, respectively, with standard deviations in the range of 10 - 15 %. Soil-corrected potassium calculated in this manner has been shown to be equivalent to water-soluble potassium[5].

The best indication that Pb and Br are motor-vehicle related is a Pb/Br ratio near three for fine particles (summertime acidic atmospheres often result in larger and more variable ratios). Figure 1 shows fine particle Pb vs Br for samples collected during the IACP study in 1985 in a residential neighborhood in Albuquerque. Figure 2 shows the corresponding result for Boise based on samples from both the EGP and FS sites. While the scale of Figure 2 is a factor of five smaller than Figure 1, the slopes are similar and near the expected value. Figure 2 suggests that Pb (or Br) will be an adequate motor vehicle tracer in Boise, although somewhat more noisy than in earlier work.

**Results**

Table I shows average values of the tracers measured at the two sites, separately for day and night, based on the 100 periods for which EOM measurements were also available. The pattern is as anticipated: (1) the concentration of the woodsmoke tracer ($K^*$) was higher at night than during the day, and was higher at the residential site than at the roadway site, and (2) the concentration of the motor vehicle tracer (Pb) was slightly higher during the day than at night, and was higher at the roadway site than at the residential site.

Table II shows the results from the equation

$$EOM_i = (117 \pm 8)\ K^*_i + (66 \pm 16)\ Pb_i + 1.7 \pm 1.1 \qquad (3)$$
$$r = 0.89,\ n = 97$$

which is based on fitting equation 1 to data from both sites together. Of 100 cases originally available, three were omitted in the fit represented by equation 3. All three were from the EGP site, the two highest measured nighttime concentrations and one small daytime concentration. Including these three cases increased both a and b by only 10 %, but with very high residuals for the three cases. Neither were included in calculating any of the values shown in Table II. There is seen to be generally good agreement between the measured EOM values and the totals resulting from the sums of the first three columns. The dominant contribution of woodsmoke at both sites is apparent.

Using Br rather than Pb gave source apportionment results generally similar to those shown in Table II, with mostly the same cases as before emerging as outliers. Treating the two sites separately however gave less consistent results. Thus while the Pb coefficients (with their uncertainties) found separately for the two sites overlapped that found for the combined data set, the Br coefficients did not. For both Pb and Br the separate site analyses gave source apportionment results which increased the motor vehicle contribution at the EGP site relative to the FS site. For all analyses, however, the woodsmoke contributions were relatively unchanged and remained dominant.

**Conclusion**

In spite of the reduced ambient concentrations of Pb since January 1986, the Boise data suggests this element is still an adequate (although more noisy) tracer of motor vehicle emissions. An MLR receptor model using Pb and soil-corrected K showed an overall dominance of woodsmoke over motor vehicles in their contributions to ambient EOM at both the residential and roadway sites. Remaining ambiguities in the source apportionment results should be

resolvable with $^{14}C$ analyses that are planned.

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Table I. Average Measured Concentrations ($ng/m^3$).

| | Elm Grove Park | | Fire Station | |
|---|---|---|---|---|
| | K* | Pb | K* | Pb |
| 0700 - 1900 | 95 | 50 | 70 | 80 |
| 1900 - 0700 | 155 | 43 | 138 | 68 |

Table II. Average Contributions to Boise Ambient EOM Concentrations ($\mu g/m^3$).

| | Wood | Mobile | Other | Total | Meas. |
|---|---|---|---|---|---|
| **Elm Grove Park** | | | | | |
| 0700 - 1900 | 11.6 ± 1.2 | 3.4 ± 0.9 | 1.7 ± 1.1 | 16.7 | 16.3 |
| 1900 - 0700 | 16.8 ± 1.7 | 2.5 ± 0.6 | 1.7 ± 1.1 | 21.0 | 23.8 |
| **Fire Station** | | | | | |
| 0700 - 1900 | 8.2 ± 0.8 | 5.3 ± 1.3 | 1.7 ± 1.1 | 15.2 | 13.4 |
| 1900 - 0700 | 16.1 ± 1.6 | 4.5 ± 1.1 | 1.7 ± 1.1 | 22.3 | 21.9 |

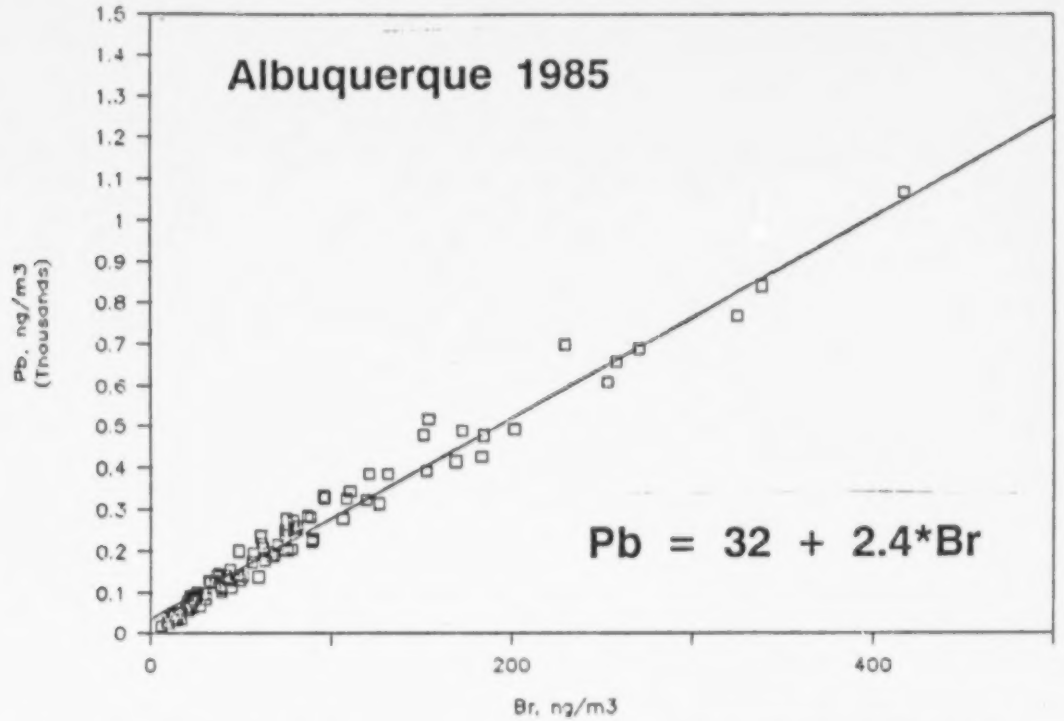


Figure 1. Fine particle Pb vs Br in Albuquerque, 1985.

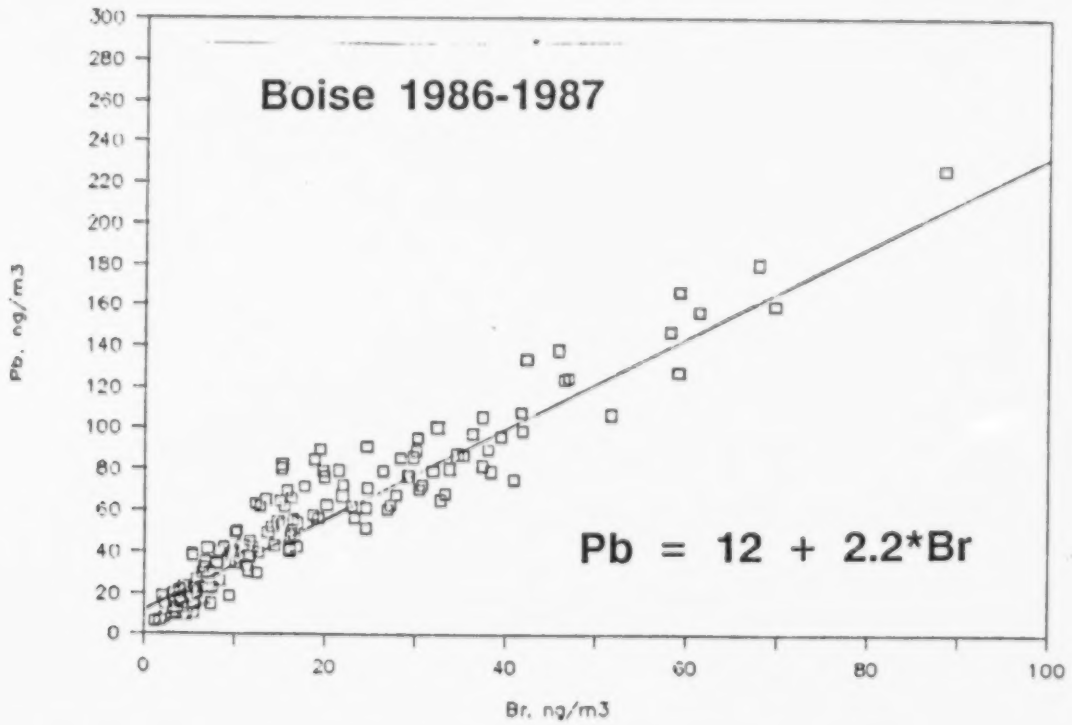


Figure 2. Fine particle Pb vs Br in Boise, 1986 - 1987.